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Ozone depletion potential of CH_3Br

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Abstract. The ozone depletion potential (ODP) of methyl bromide (CH_3Br) can be determined by combining the model-calculated bromine efficiency factor (BEF) for CH_3Br and its atmospheric lifetime. This paper examines how changes in several key kinetic data affect BEF. The key reactions highlighted in this study include the reaction of BrO + HO_2, the absorption cross section of HOBr, the absorption cross section and the photolysis products of $BrONO_2$, and the heterogeneous conversion of $BrONO_2$ to HOBr and HNO_3 on aerosol particles. By combining the calculated BEF with the latest estimate of 0.7 year for the atmospheric lifetime of CH_3Br, the likely value of ODP for CH_3Br is 0.39. The model-calculated concentration of HBr (~0.3 pptv) in the lower stratosphere is substantially smaller than the reported measured value of about 1 pptv. Recent publications suggested models can reproduce the measured value if one assumes a yield for HBr from the reaction of BrO + OH or from the reaction of BrO + HO_2. Although the *DeMore et al.* [1997] evaluation concluded any substantial yield of HBr from BrO + HO_2 is unlikely, for completeness, we calculate the effects of these assumed yields on BEF for CH_3Br. Our calculations show that the effects are minimal: practically no impact for an assumed 1.3% yield of HBr from BrO + OH and 10% smaller for an assumed 0.6% yield from BrO + HO_2.

1. Introduction

Current measurements of the organic bromine compounds in the upper troposphere and lower stratosphere have confirmed that CH_3Br is the major contributor to stratospheric bromine loading [see, e.g., *Wamsley et al.*, 1998]. The ozone depletion potential (ODP) of CH_3Br provides a measure of the expected effect on stratospheric ozone from emission of CH_3Br to the atmosphere. The ODP of CH_3Br is a function of the number of bromine radicals delivered to the stratosphere per unit mass of CH_3Br emitted at the ground and the ozone removal efficiency of the released bromine radicals. Analysis of the former is complicated by the large uncertainties associated with the atmospheric lifetime of CH_3Br. Apart from its removal by reaction with OH in the atmosphere, CH_3Br is also removed by deposition to soil and oceans. Although the impact of bromine chemistry on stratospheric ozone has been studied for close to 2 decades [see *World Meteorological Organization* (*WMO*), 1995], our knowledge of atmospheric bromine is still limited by the lack of direct observations of some of the bromine radicals and reservoir species in the stratosphere. With BrO being the only bromine species observed in aircraft campaigns, the type of process studies that can be used to verify our understanding of the partitioning in the atmosphere is limited. The recently reported measured HBr concentration of about 1–1.5 pptv [*Nolt et al.*, 1997; *Carlotti et al.*, 1995; *Johnson et al.*, 1995; *Park et al.*, 1989] in the lower stratosphere further complicated the picture as models are not able to reproduce this value with current rate data recommendations.

Changes in the values of the ODP of CH_3Br in the past have resulted from changes in both reaction rate constants for bromine radicals and changes in the atmospheric lifetime of CH_3Br. In this paper, we review how the calculated ODP for CH_3Br has changed with particular emphasis on the recent changes due to the revised rate constants of *DeMore et al.* [1997] (hereinafter referred to as JPL-97).

2. ODP for CH_3Br

The ozone depletion potential (ODP), first introduced by *Wuebbles* [1983], is now extensively used by policy makers as a simple relative measure to assess the potential impact of a given compound on the stratospheric ozone layer. The ODP is calculated relative to CFC-11 and depends principally on two major factors: (1) the bromine loading potential (BLP) which measures the amount of bromine radicals delivered to the stratosphere per unit mass emitted at the ground, and (2) the bromine efficiency factor (BEF) which measures the relative catalytic efficiency of the radicals in stratospheric ozone removal.

The bromine loading potential (BLP) reflects the amount of inorganic bromine added to the stratosphere from a given emission. An estimate for the amount of inorganic bromine present in the stratosphere due to continuous emission of a particular bromine-containing compound with a lifetime longer than several months is given by the steady state tropospheric concentration of the compound multiplied by the num-

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Table 1. Values of ODP for CH_3Br

Circa	Rate Data	BEF	Key Revisions	τ_{rec}, years	Comment	ODP
1992	JPL-90	36	...	2.1	removal by OH only	0.73
1992	JPL-92	49	BrO + HO_2 10 times faster	2.1	removal by OH only	0.99
1994	JPL-94	48	...	1.3	include removal by ocean	0.60
1994	JPL-94*	44	JPL-94 + HOBr cross section from *Orlando and Burkholder* [1995]	1.3	include removal by ocean	0.55
1997	JPL-97	58	see Table 2	0.7	include removal by soil and biological removal in ocean water	0.39

ber of bromine atoms per molecule. At steady state (i.e., when additions to the atmosphere equal removal from the atmosphere), the estimate for inorganic bromine concentration in parts per billion by volume (ppbv) is given by $[Br_y]_{ss_x} = E_{ss_x}\tau_x N_{Br} A_x$, where N_{Br} is the number of bromine atoms per molecule of compound x, τ_x is the atmospheric lifetime of compound x, E_{ss_x} is the steady state emissions in mass per unit time, and A_x is

$$A_x = \frac{\mu_{air}}{\mu_x} \times \frac{1}{\text{mass of the atmosphere}} \times 10^9$$

where μ is molecular weight in grams and the mass of the atmosphere is 4.8×10^{21} grams. The BLP is the ratio of the steady state concentration of bromine released by compound x for a given emission rate to the steady state concentration of chlorine released by CFC-11 for an equal (by mass) emission rate:

$$BLP_x = \frac{\left[\frac{\tau N_{Br}}{\mu}\right]_x}{\left[\frac{\tau N_{Cl}}{\mu}\right]_{CFC\text{-}11}}. \quad (1)$$

The ODP is defined as the ratio of the ozone depletion produced by a unit-mass emission of compound x to the ozone depletion produced by a unit-mass emission of CFC-11 (the traditional reference gas). Numerical models that incorporate the pertinent chemistry and trace gas transport of the atmosphere are used to compute the ODP. For such modeling exercises the steady state ODP for compound x can be given by [*Fisher et al.*, 1990]:

$$ODP_x = \frac{\text{calculated steady state ozone depletion of about 1\% due to } x}{\text{emission rate of } x \text{ to produce this decrease of ozone in the model}} \Big/ \frac{\text{calculated steady state ozone depletion of about 1\% due to CFC-11}}{\text{emission rate of CFC-11 to produce this decrease of ozone in the model}} \quad (2)$$

where 1% depletion is required to yield results above model noise levels but within the region of linear model response. The ratio BEF_x, defined by $[ODP/BLP]_x$ is a measure of the relative ozone removal efficiency of the bromine radicals delivered to the stratosphere. In the definition the behavior of CFC-11 is used as the reference standard. The value of BEF corresponds to the spatial and seasonal average of the local ozone removal efficiency of the bromine radicals released by x relative to the chlorine atoms released by CFC-11. Note that the BEF value is species dependent; that is, if two species release bromine radicals at different locations in the lower stratosphere, the BEF values will be different for the two species.

Because of differences in model formulation, different models will calculate slightly different atmospheric lifetimes. This is further complicated by the fact that some species are affected by surface removal processes that are difficult to model. Previous analyses [see, e.g., *Solomon et al.*, 1992] have shown that the model-calculated BEF_x depends on the local stratospheric lifetime of the source gas. Changes in lifetimes due to tropospheric and surface processes would not affect BEF_x as long as they are not so fast that the mixing ratio of the source gas becomes nonuniform in the troposphere. Making use of this property, one can assign an ODP value using the standard recommended lifetime (τ_{rec}) as follows

$$(ODP)_{\tau_{rec}} = (BLP)_{\tau_{rec}} BEF_x \quad (3)$$

where $(BLP)_{\tau_{rec}}$ is defined as in (1) using recommended lifetimes for x and CFC-11.

Table 1 summarizes how the calculated values of ODP for CH_3Br have changed since 1990. These values are calculated by the Atmospheric and Environmental Research, Inc. (AER) model using different rate constants as available at the time. Between 1990 and 1997 the BEF for CH_3Br has increased, while its lifetime has decreased. On balance, the ODP has decreased from 0.99 to 0.39.

3. Atmospheric Lifetime of Methyl Bromide

The net atmospheric lifetime (τ_{tot}) for methyl bromide is given by

$$\frac{1}{\tau_{tot}} = \frac{1}{\tau_{gas}} + \frac{1}{\tau_{ocean}} + \frac{1}{\tau_{land}}$$

In the above expression, τ_{gas} denotes the lifetime against atmospheric removal by gas-phase reactions and photolysis of CH_3Br and is defined by the total column density (cm^{-2}) divided by the integrated loss rate ($cm^{-2}\ s^{-1}$) over the whole atmosphere. The lifetime against ocean uptake, τ_{ocean}, is defined as the methyl bromide atmospheric burden divided by the flux into the ocean. A similar definition holds for the lifetime against uptake by land surfaces, τ_{land}.

Although photolysis and reactions of CH_3Br with $O(^1D)$, $O(^3P)$, NO_3, and Cl take place in the atmosphere, gas-phase removal of methyl bromide is likely to be dominated by its reaction with tropospheric OH. On the basis of the latest recommended rate constants of the reaction of CH_3Br with OH, and of CH_3CCl_3 with OH, together with the most recent

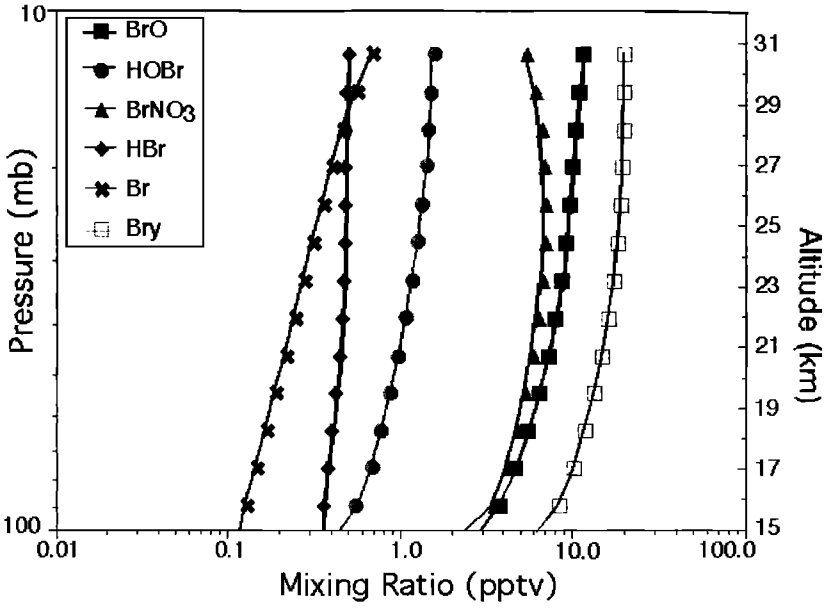

Figure 1. Model-calculated daytime averaged mixing ratio profiles for spring conditions at 38°N latitudes. The calculations were performed using JPL-97 rate recommendations.

analysis of Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment (ALE/GAGE) data [*Prinn et al.*, 1995], a partial lifetime due to reaction with OH in the troposphere for CH_3Br of 1.9 ± 0.4 years, is derived. When combined with the partial lifetime due to stratospheric removal, the estimated τ_{gas} is 1.8 years.

Hydrolysis and reaction with chloride ions in seawater constitute an important sink for atmospheric CH_3Br. This is in contrast to halocarbons and proposed substitutes which, due to low solubility (typically $H \sim 10^{-2}$ mol L^{-1} atm^{-1}) and slow aqueous degradation rates (typically $k_w \sim 10^{-9}$ s^{-1}), have ocean uptake lifetimes of the order of hundreds of years [*Wine and Chameides*, 1990]. *Butler* [1994] described a method to calculate the (partial) atmospheric lifetime of CH_3Br due to removal by the ocean (τ_{ocean}) in terms of the surface mixed layer depth of the ocean, sea surface temperature, wind speed, thermocline diffusivity, solubility of CH_3Br in seawater, and degradation rate coefficient in seawater. The *Butler* [1994] estimate was carried out using a two-box model so that weighted averages of the parameters were used in the calculations. The calculated best estimate for τ_{ocean} was 3.7 years, with a possible range from 1.4 year to 14 years. These values were adopted by the *WMO* [1995] report. The same methodology was used by *Yvon and Butler* [1996] but with the parameters calculated individually for each 2° by 2° grid over the oceans. Thus they were able to take into account the covariations of the parameters before summing the effects to obtain the global partial lifetime. With this method they obtained a best estimate for τ_{ocean} of 2.7 years, with a range from 2.4 to 6.5 years. The latest update [*Yvon-Lewis and Butler*, 1997] includes biological removal and lowers the lifetime to 1.8 years, with a range from 1.1 years to 3.9 years.

In situ measurements of deposition velocity of CH_3Br over land are not available. On the basis of the uptake rates measured for five types of soil, *Shorter et al.* [1995] computed the partial lifetime of CH_3Br. The value is based on the sum of the annual uptake fluxes (g yr^{-1}) by the five soil types, each of which is estimated as the product of the uptake rate for the soil type (g m^{-2} d^{-1}), the area of the soil type on the globe (m^2), and the number of active days in a year (d yr^{-1}). The five soil types were assigned two uptake rates, corresponding to deposition velocities of 0.12 cm s^{-1} and 0.02 cm s^{-1}. The value obtained due to soil removal is 3.4 years. Combining the three partial lifetimes provides a best estimate of 0.7 years.

4. Partitioning of the Bromine Radicals

We used the AER two-dimensional (2-D) model [*Weisenstein et al.*, 1996] with the standard JPL-97 reaction rate constants for the gas-phase reactions and parameterization for heterogeneous reactions on sulfate aerosol. Following the method used by *WMO* [1992], the ODP is calculated based on a background chlorine and bromine concentration of 3.5 ppbv and 19 pptv, respectively.

The concentrations of the bromine radicals at 38°N for spring conditions calculated using JPL-97 recommended rate constants are shown in Figure 1. Note that at that latitude, $BrONO_2$ and BrO are the most abundant species. The concentrations of HOBr and HBr are less than 1 pptv. Figures 2a and 2b show the computed [BrO]/[Br_y] ratio. It is evident that the BrO concentrations calculated using JPL-97 are larger than those calculated using *DeMore et al.* [1994] (hereinafter referred to as JPL-94). This accounts for the larger BEF in Table 1. Values for [BrO]/[Br_y] ratio derived by *Avalone et al.* [1995] from observations are included in the figure for comparison. However, it should be noted the partitionings were calculated in the model without constraining ozone and other species to the observed values. Thus the fact that results calculated using JPL-94 agree better with the derived values does not necessarily imply that there is a problem with the JPL-97 recommendations.

The reported measured concentration of 1.5 pptv for HBr between 25 and 35 km [*Carlotti et al.*, 1995] is much larger than the model-computed value of about 0.3 pptv. In section 6 we

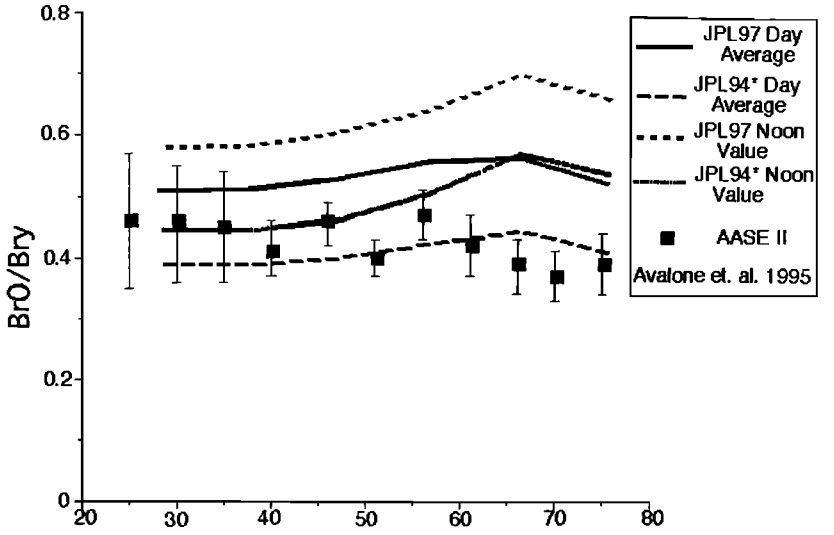

Figure 2a. Comparison of model-calculated values of the [BrO]/[Bry] ratio compared with the values derived from the AASE II measurements as reported by *Avalone et al.* [1995]. The model values are for northern hemisphere at 20 km altitude and are taken from the 2-D CTM computed using model-calculated values of Bry and ozone. The results are sorted by latitudes.

will discuss ways of increasing the calculated concentration of HBr in the model and how they affect BEF.

5. Sensitivity of BEF to Selected Rate Data

The following reactions represent the primary bromine-driven catalytic ozone removal cycles in the stratosphere:

Cycle 1

$$\left.\begin{array}{l} ClO + BrO \rightarrow BrCl + O_2 \\ BrCl + h\nu \rightarrow Br + Cl \\ Br + O_3 \rightarrow BrO + O_2 \\ Cl + O_3 \rightarrow ClO + O_2 \end{array}\right\} \overline{2O_3 \rightarrow 3O_2}.$$

Cycle 2

$$\left.\begin{array}{l} BrO + HO_2 \rightarrow HOBr + O_2 \\ HOBr + h\nu \rightarrow OH + Br \\ Br + O_3 \rightarrow BrO + O_2 \\ OH + O_3 \rightarrow HO_2 + O_2 \end{array}\right\} \overline{2O_3 \rightarrow 3O_2}.$$

Cycle 3

$$\left.\begin{array}{l} BrO + O \rightarrow Br + O_2 \\ Br + O_3 \rightarrow BrO + O_2 \end{array}\right\} \overline{O + O_3 \rightarrow 2O_2}.$$

Cycle 4

$$\left.\begin{array}{l} 2(Br + O_3 \rightarrow BrO + O_2) \\ BrO + BrO \rightarrow 2Br + O_2 \end{array}\right\} \overline{2O_3 \rightarrow 3O_2}.$$

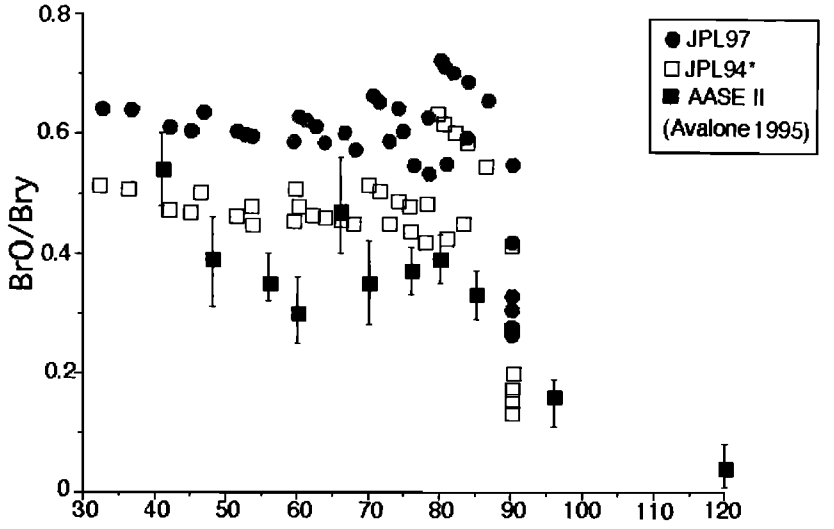

Figure 2b. Same as Figure 2a, except that the results are sorted by solar zenith angles.

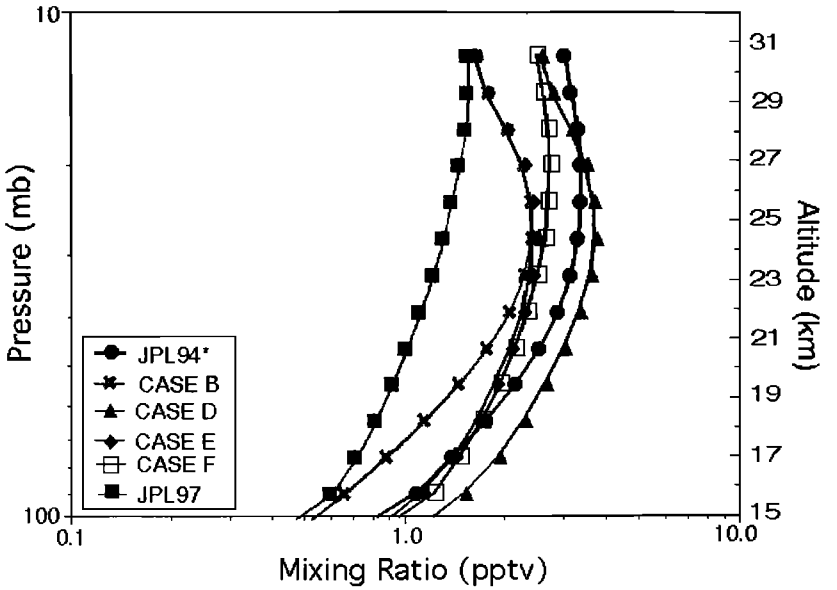

Figure 3. Model-calculated daytime average concentration of HOBr for different cases. See Table 3 for the description of the cases.

Cycle 5

$$\left.\begin{array}{r} BrNO_3 + h\nu \rightarrow Br + NO_3 \\ NO_3 + h\nu \rightarrow NO + O_2 \\ Br + O_3 \rightarrow BrO + O_2 \\ NO + O_3 \rightarrow NO_2 + O_2 \\ BrO + NO_2 + M \rightarrow BrNO_3 + M \end{array}\right\}$$
$$\overline{2O_3 \rightarrow 3O_2}.$$

Current rate constants indicate that in the present day atmosphere the first three cycles contribute about an equal amount to ozone depletion in the lower stratosphere, with the last two about an order of magnitude smaller. Alternative product channel for the reaction of BrO with ClO includes production of OClO and ClOO. Photolysis of these products results in null cycles with no impact on ozone depletion. Reactions of OClO with O or OH would lead to ozone depletion cycles. Thus titration of ClO to OClO could, in principle, affect the ODP. However, the effect is small.

Reaction (R1) ($BrO + HO_2 \rightarrow HOBr + O_2$) represents the rate-limiting steps in cycle 2. Changes in BEF prior to JPL-94 recommendation (see Table 1) can be understood in terms of changes in the rate constant for (R1) and the HOBr absorption cross sections. With an estimated temperature dependence the rate recommended by *DeMore et al.* [1992] (hereinafter referred to as JPL-92) based on room temperature value by *Poulet et al.* [1992] is about a factor of 10 faster at stratospheric temperatures than that recommended by *DeMore et al.* [1990] (hereinafter referred to as JPL-90). As a result of this revision, the BEF increases from 37 to 49. In the JPL-94* calculation we included the absorption cross section for HOBr as reported by *Orlando and Burkholder* [1995], which is the first laboratory-measured absorption cross section for HOBr. Prior to that, the much larger cross section of HOCl was used as a proxy, resulting in computed HOBr concentration of less than 0.1 pptv at 16 km and 0.8 pptv at 30 km. With the Orlando and Burkholder cross section the concentration of HOBr is around 1 pptv at 16 km and 3 pptv around 30 km (see the curve labeled JPL-94* in Figure 3), comparable to those of BrO and $BrONO_2$. Inclusion of this cross section makes HOBr a more important reservoir species and lowers the BEF from 49 to 44.

To illustrate how changes in rate constants from the JPL-97 recommendation affect BEF, we summarize the key revisions between the JPL-94* and JPL-97 in Table 2. Changes to reactions (R1) through (R8) impact the ozone removal efficiency either directly because they are the rate-limiting step in the cycle, or indirectly by changing the partitioning between BrO and the reservoir species. We explore the dependence by performing a series of calculations to obtain the BEF in each case. The results are summarized in Table 3.

Many of the reactions in Table 2 affect BEF through calculated changes in the concentrations of HOBr. Compared to the profile calculated using JPL-94* rates, the smaller rate constant for (R1) results in smaller HOBr (see case B in Figure 3). The heterogeneous reaction (R3) convert $BrONO_2$ to HOBr and BrO. As a result of this reaction, both HOBr and BrO are larger (see case D in Figure 3). The combined effect of (R1) and (R3) is represented in Figure 3 as case E. To isolate the effects of changes in photolysis cross sections, we performed case F where we have updated all the JPL-97 rate data except the absorption cross sections. The value obtained in the lower stratosphere is similar to case E. The difference between case E and case F around 30 km is the result of the slower rate for (R8) (O + HOBr) in the JPL-97 recommendation. Figure 4 shows the absorption cross sections of HOBr from *Orlando and Burkholder* [1995] and the JPL-97 recommendation. As noted in JPL-97, the recommended cross section is influenced by the measurements reported by *Rattigan et al.* [1996]. With the larger cross section between 300 and 400 nm and the extension of the cross section beyond 400 nm, the photolysis rate of HOBr is 3 times larger in the lower stratosphere leading to a smaller concentration of HOBr (see cases F and JPL-97 in Figure 3).

We will now discuss the effects of the rate revisions on the model-calculated BEF for CH_3Br. The *Orlando and Burkholder* [1995] cross section for HOBr decreases the sensitivity of the model-calculated BEF to changes in the reaction rate

Table 2. Summary of Rate Revisions for Key Bromine Chemistry Reactions in JPL-97

Rate*	JPL-97	JPL-94	Remark
(R1): BrO + HO_2	3.4×10^{-12} exp (540/T)	6.2×10^{-12} exp (500/T)	new rate is 0.65 times old rate at 230 K
(R2a): absorption cross section of $BrONO_2$	temperature dependent cross section extended to longer wavelengths		new J rate is 1.25 times larger than the old one
(R2b): quantum yield	$\Phi_{BrO+NO_2} = 0.71$, $\Phi_{Br+NO_3} = 0.29$	$\Phi_{BrO+NO_2} = 0$ $\Phi_{Br+NO_3} = 1.0$	cycle 5 is 0.3 times smaller
(R3): heterogeneous conversion of $BrONO_2$ on sulfate	temperature dependent rate with γ as large as 0.8	no recommendation	
(R4): photolysis of HOBr	larger cross section at long wavelengths		new J rate is a factor of 3 larger than old
(R5): BrO + O	1.9×10^{-11} exp (230/T)	1.7×10^{-11} exp (260/T)	new rate 0.98 times old rate at 230 K
(R6): BrO + BrO	1.5×10^{-12} exp (230/T)	4.0×10^{-12} exp (−190/T) 4.2×10^{-14} exp (660/T)	new rate is 1.6 times old rate at 230 K
(R7): BrO + OH	7.4×10^{-11}	1×10^{-11} (estimated)	
(R8): O + HOBr	1.2×10^{-10} exp (−430/T)	2.5×10^{-11} (at 298 K)	

*Rate constants for bimolecular reactions are in units of cm^3 $molecule^{-1}$ s^{-1}.

constant for (R1). With HOBr being a major reservoir, any increase (decrease) in k_1 is compensated by decrease (increase) in [BrO] so that the change in the rate-limiting step k_1[BrO][HO_2] will be smaller than the corresponding change in k_1. This is illustrated by the results for case B in Table 3. Despite a factor of 2 decrease in the rate constant for (R1), the BEF for case B is practically the same as that for case A. Reaction (R3) is a major source of HO_x in the lower stratosphere via production of HOBr and its subsequent photolysis [*Danilin and McConnell*, 1995; *Lary et al.*, 1996]. The reaction also leads to a higher concentration of BrO and smaller concentration of NO_x. The additional source of HO_x and smaller NO_x enhance the ClO_x and HO_x ozone removal cycles. Cases D shows a 19% increase in the BEF. Our diagnostics reveal increased contributions from cycles 1 and 2 where a larger reservoir of HOBr and BrO are produced via reaction (R3). The combined effects of (R1), (R2b), and (R3) are given in case E. The resulted BEF can be compared with that for case F, which consists of all JPL-97 updates excluding the cross sections. The similarity in BEF for the two cases shows that the effects of (R5) through (R8) on BEF are small.

The final four cases in Table 3 illustrate the contributions of the cross section revisions on BEF. Within this group, modification to the HOBr absorption cross section has the largest effects. The larger cross section leads to higher concentrations of BrO and larger BEF. Revision of the $BrONO_2$ cross section involves both the magnitude and the product yield. The measurement reported by *Burkholder et al.* [1995] extends the measured values to beyond 390 nm. With the new cross section the photolysis rate is a factor of 1.25 larger in the lower stratosphere leading to higher concentrations of BrO and BEF (see case F and case H). For $BrONO_2$ photolysis (R2), only Φ_{Br+NO_3} leads to ozone destruction as the Φ_{BrO+NO_2} branch is a null cycle. Previously, it has been assumed that $\Phi_{Br+NO_3} = 1$ with $\Phi_{BrO+NO_2} = 0$. The JPL-97 recommends $\Phi_{Br+NO_3} = 0.29$ with $\Phi_{BrO+NO_2} = 0.71$ based on work of S. Nickolaisen and S. Sander (private communication, 1998). *Harwood et al.* [1998] examined the quantum yields at three wavelengths. Their results showed that $\Phi_{Br+NO_3} = 0.28$ at 245 nm, and near unity at 308 nm and 352.5 nm with an uncertainty of about 35%. Our diagnostics reveals that the cycle 5 contribution is small compared to the other cycles around 20 km. Thus the effect of the change in branching on BEF is small as illustrated by case C. The cross-section revisions for BrCl and quantum yield for $ClONO_2$ are each responsible for increasing the BEF by 0.5 to bring the BEF to 58 in case J.

Table 3. Model-Calculated BEF Using Different Input

	Comment	BEF
Case A	JPL-94*	44
Case B	JPL-94* + (R1)	43
Case C	JPL-94* + (R2b)	43
Case D	JPL-94* + (R3)	54
Case E	JPL-94* + (R1) + (R2b) + (R3)	49
Case F	JPL-97 except all photolysis absorption cross sections are from JPL-94*	49
Case G	case F + HOBr cross section from JPL-97	54
Case H	case F + $BrONO_2$ cross section from JPL-97	52
Case I	case F + HOBr and $BrONO_2$ cross section from JPL-97	57
Case J	JPL-97	58

JPL-94* uses *Orlando and Burkholder* [1995] cross section for HOBr.

6. ODP and BEF of CH_3Br With HBr Concentrations at 1.5 pptv

The calculated concentration of HBr in Figure 1 is much smaller than values reported in the literature. To obtain cal-

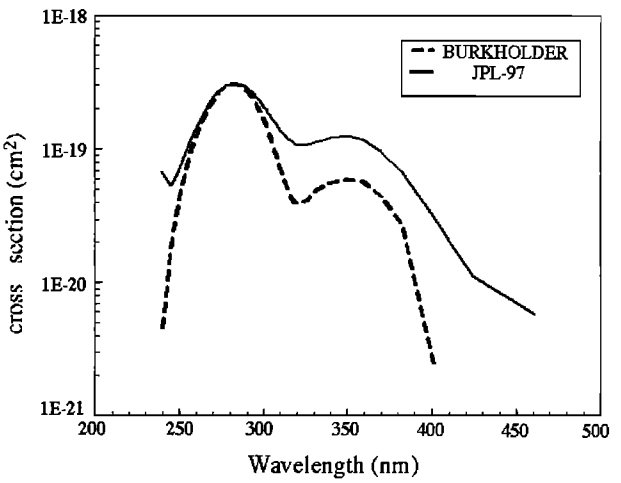

Figure 4. Absorption cross sections of HOBr from *Orlando and Burkholder* [1995] and the JPL-97 recommendation.

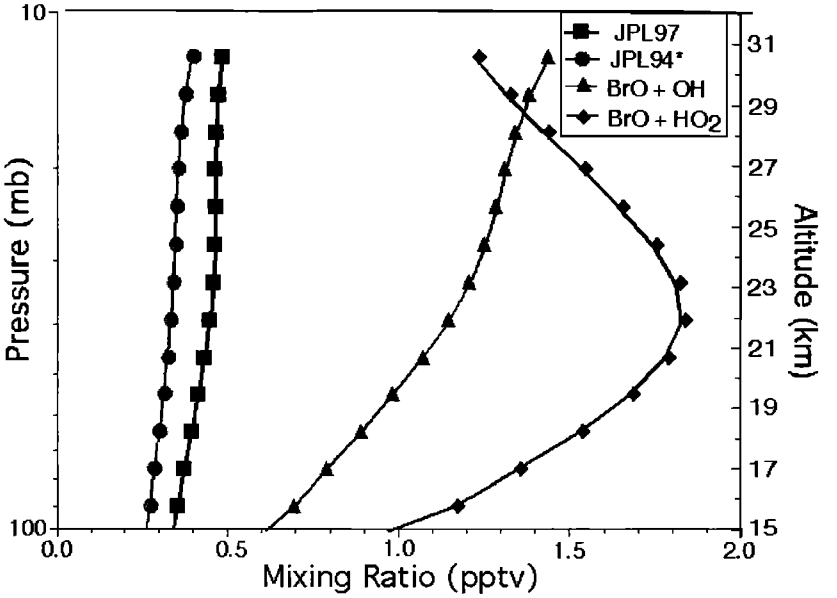

Figure 5. Model-calculated mixing ratio profiles for HBr calculated using JPL-94 and JPL-97 rate data recommendations. The curve labeled BrO + OH is calculated assuming an HBr yield of 1.3% from the reaction. The curve labeled BrO + HO_2 assumes an HBr yield of 0.6% from the reaction.

culated concentrations of HBr similar to recent measured values of HBr in the lower stratosphere by *Carlotti et al.* [1995] and *Nolt et al.* [1997], alternative mechanisms that would produce HBr have been suggested.

Several studies [*Larichev et al.*, 1995; *Mellouki et al.*, 1994] indicated that the product of (R1) is HOBr and O_2, although it is not possible to confirm or refute a small yield of HBr by direct measurements. *Mellouki et al.* [1994] estimated an upper limit of 0.01% for HBr yield based on studies of the HBr + O_3 reaction. Another possible source of HBr is from the reaction of BrO with OH. Two recent publications presented model results to show how a small yield from BrO + OH [*Chipperfield et al.*, 1997] or yields from either reactions [*Chartrand and McConnel*, 1998] could successfully simulate the measured concentration. While it is unlikely that HBr could be produced from the reaction of BrO with HO_2, for completeness, we calculate the ODP for CH_3Br assuming a 1.3% yield of HBr from BrO + OH, or an HBr yield of 0.6% from BrO + HO_2 in two separate cases. Annual averages of HBr between 25 and 35 km are calculated to be 1.3 and 1.5 pptv for the two cases, respectively (see Figure 5). In both cases, HBr is elevated by over 100% from case A. The concentrations of the remaining bromine species are decreased by up to 10%. The effect on BEF is small as evident from the small changes in BrO in Figure 6. The calculated BEF values are 56 (for the BrO + OH case) and 52 (for the BrO + HO_2) case, compared to a value of 58 calculated with no assumed HBr yield. Our calculations show that suggested ways to increase model-calculated HBr in the published literature have only a small effect (about 10%) on the ODP.

7. Concluding Remarks

The calculated ODP for CH_3Br can be considered as the products of two factors (BEF and atmospheric lifetime) that are almost independent of each other. The BEF depends on stratospheric chemistry that determines the distributions and reactivities of the chlorine and bromine radicals in the stratosphere. The atmospheric lifetime of CH_3Br is controlled mainly by processes in the troposphere. In this paper, we discussed the sensitivity of BEF to several bromine reactions that have direct impacts on the concentration of BrO and HOBr, and whose rate constants have been revised in the JPL-97 recommendation. We did not explore the sensitivity of BEF to uncertainties in other rate data. We acknowledge that this is an important issue, but it is beyond the scope of the present work. Since BEF is defined relative to the ozone removal efficiency of chlorine radicals, a full analysis will require identifying the key reactions that will both maximize and minimize the ozone depletions from both chlorine and bromine radicals and the coupling among those terms. A possible approach is to use the Monte Carlo method where the reaction rate constants are randomly varied based on the reported uncertainties [*Stolarski and Douglass*, 1986]. As indicated by *Stolarski and Douglass* [1986], such an approach is only meaningful if one could identify a set of observations to reject certain combinations of extreme values in order to get a meaningful range. This would seem a particularly daunting task given the paucity of observations for the bromine radicals. Our subjective estimate for the uncertainty in BEF due to the overall uncertainties in rate data is at least 30%.

Although observations of BrO in the lower stratosphere and the tentative upper limits on HBr above 30 km place some constraints on bromine chemistry, they do not rule out models which assume a small (~1%) HBr branching. Our analysis showed that the effect on BEF from the two mechanisms identified in the published literature is small, decreasing by less than 10%. Laboratory studies together with selective (but more frequent) stratospheric measurement (e.g., simultaneous measurement of BrO and HBr over an extended (20–30 km) altitude region) will help expand our understanding of stratospheric bromine chemistry. The key reactions include heterogeneous reactions of $BrONO_2$ (with H_2O (reaction (R3)) and

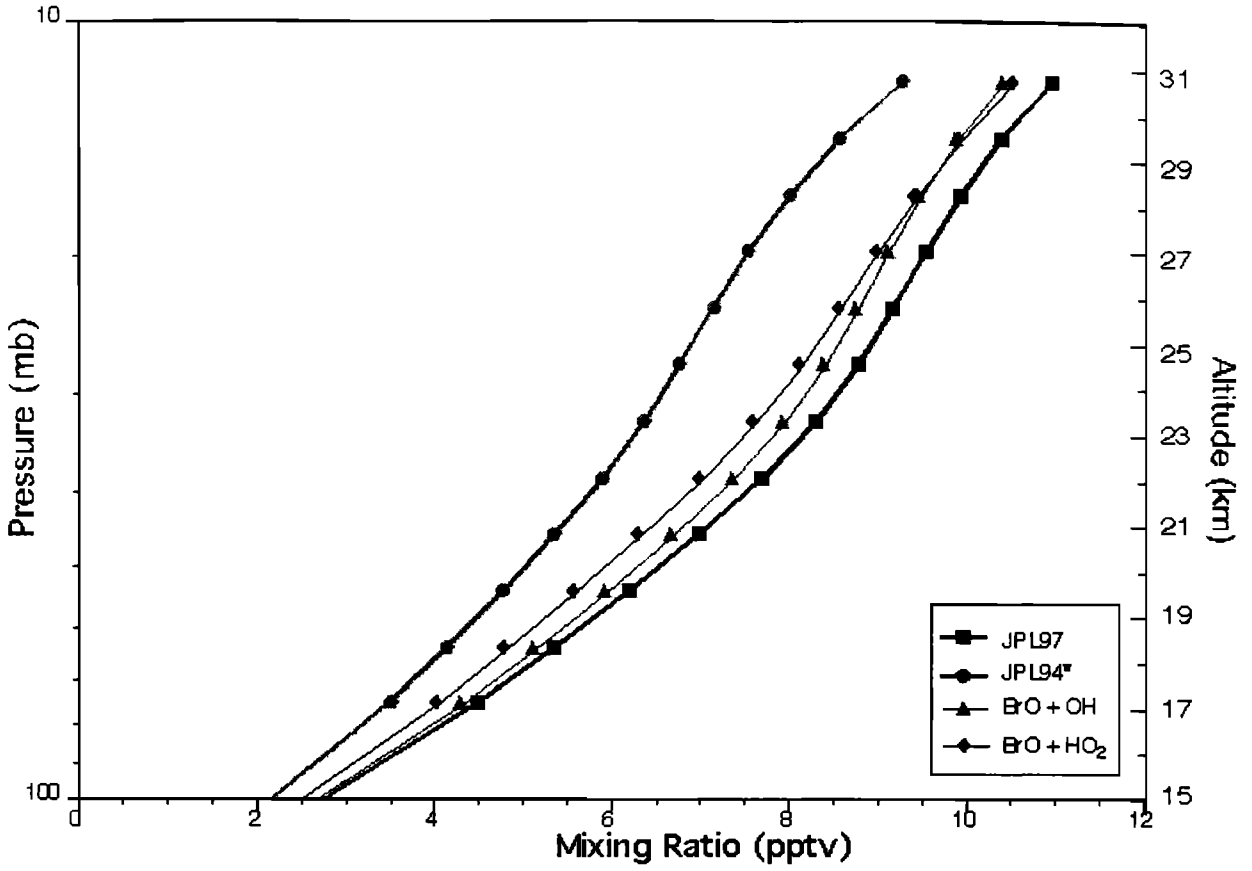

Figure 6. Same as Figure 5, except for BrO.

HCl); absorption cross sections and quantum yield of $BrONO_2$ (reaction (R2)) and HOBr (reaction (R4)); and possible alternative production mechanisms for HBr (reactions (R1) and (R2) plus others).

The possibility of missing chemistry should not be overlooked. A recent report by *Renard et al.* [1997] attributed certain spectral features in their UV/visible spectrum from nighttime balloon flights to OBrO. Assuming that the absorption cross sections at the band peaks for OBrO are the same as those for OClO, *Renard et al.* [1997] derived nighttime concentration of OBrO in the range of 10–30 pptv. This would imply that OBrO is the major nighttime reservoir of Bry. Recent work by *Chipperfield et al.* [1998] used estimated rate data to explore various production mechanisms for OBrO and concluded that the maximum nighttime concentration of OBrO in the lower stratosphere is likely to be only around 0.01 pptv. As discussed by *Chipperfield et al.* [1998], available kinetic data indicate that OBrO is most likely formed by reaction of BrO + O_3 and removed by photolysis, producing BrO + O. This sequence of reaction is a null cycle for ozone removal. Thus these reactions associated with OBrO will have no direct effect on the ODP of CH_3Br. However, if OBrO is a major reservoir during the day, the concentrations of BrO and HOBr would be smaller, decreasing the ODP. The resolution of the role of OBrO in bromine chemistry awaits reliable kinetic data.

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